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**Author:** Krystyna Kozioł, Marek Ruman, Katarzyna Kozak, Żaneta Polkowska

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# Release and Transport of Toxic, Mobile Organic Compounds (Formaldehyde and Phenols) on an Arctic Glacier

Krystyna Kozioł[a,*], Marek Ruman[b], Katarzyna Kozak[a] and Żaneta Polkowska[a]

[a] *Department of Analytical Chemistry, The Chemical Faculty, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland*

[b] *Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland*

**Abstract**

As a result of current deglaciation, the chemical cycles of many compounds, including toxic formaldehyde and phenols, are changing. However, the processes by which these chemicals are released have yet to be studied *in situ*. Here, we quantify fluxes of HCHO and phenols in a glacial catchment within one summer season, obtaining a net release from the glacier of $0.106 \cdot 10^6$ g formaldehyde and $0.255 \cdot 10^6$ g phenols, which can be interpreted as a combined result of summer deposition and glacier ice melt. Formaldehyde flux was shown to increase by 164% on a 250 m stretch of the stream flowing through an icing (an exposed former glacier bed area), whilst phenols have shown a smaller increase of 48%. Hence, the importance of glacial forefields in chemical cycle of toxic compounds is pronounced and requires further attention.


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*Keywords:* Formaldehyde, phenols, ice, glacier forefield

## 1. Introduction

Arctic glaciers currently undergo rapid melting [1], [2], upon which they release organic matter influencing downstream ecosystems in two ways: supporting them with labile organic carbon as a nutrient [3] and discharging toxic organic compounds [4].

* Corresponding author. Tel.: +447522787742.
*E-mail address*: k.a.koziol@gmail.com.


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Potentially harmful compounds include formaldehyde and phenols [5], which also represent different levels of solubility in water, both being considerably mobile species. Formaldehyde is known to be produced in snowpack and upon photolysis to release OH radicals, influencing the atmospheric lifetime of many chemicals. When incorporated into ice, its concentrations can be used to draw conclusions regarding the past atmosphere oxidizing properties (e.g. [6]). Whilst the snow-atmosphere exchange has been studied thoroughly to obtain information on the ice core record interpretation [7], the processes of release from snowpack upon melt and subsequent *in situ* refreezing into superimposed ice, or removal with meltwater have yet to be studied. This will aid further understanding of its mobility in times of rapid glacier melt.

Phenols originate not only from industrial sources, but also from plant lignin [8], and have been reported in glacial settings (e.g. [3]). The behaviour of phenols upon ice formation has only been studied in laboratory conditions [9], yet on a glacier environmental agents would also play a role, such as glacial ecosystem activity [10], [11] and interactions with mineral grains. Therefore, to assess the impact on ecosystems of the formaldehyde and phenols released from glaciers, an *in situ* study is crucial.

Here, we assess the fluxes of formaldehyde and phenols in proglacial watercourses for the first time, and compare those to the content of both compounds supplied with snow. In doing so, we gain an insight into the release of these potentially toxic chemicals from glacial ice. An estimate of the temporary capture into superimposed ice is also presented in this paper.

## 2. Methods

The samples were collected on Foxfonna, a small cold-based glacier located near Longyearbyen in Svalbard. In total, 13 snow cores and 38 meltwater samples were taken between 12$^{th}$ June and 16$^{th}$ August 2012. Meltwater was sampled on a proglacial river (F1 site, 18 samples) and two proglacial streams directly at the glacier snout that merge into this river after 250 m stretch of flow through an icing (F2 and F3, 10 samples at each site).

In the field, snow water equivalent (SWE) measurements were taken for each snow sample using spring balance. The discharge (Q) in all sites at the time of sampling was measured using the salt dilution technique; the proglacial river was also monitored continuously for water level. The monitoring results will be described further in a forthcoming paper on organic carbon balance of the Foxfonna glacier.

Stream and river water was collected in the field using 1L HDPE bottles, triple rinsed with the sample. Snow cores were taken using a Kovacs 9 cm aluminum ice corer, operated manually and washed with 18 MΩ water before each use. The samples were then collected into pre-washed zip-lock bags, melted in temperature <10°C, and an aliquots of agitated samples were stored in 4°C until analysis.

Both formaldehyde and phenols concentrations were determined using spectrophotometry (Spectroquant PHARO 100, MERCK), with detection limits (LOD) of 0.02 $mg \cdot L^{-1}$ and 0.025 $mg \cdot L^{-1}$, respectively. As quality assurance we employed blank checks, standard solution analysis and triplicate sample runs.

Fluxes were estimated using averaged concentration (c) of a particular species and Q sums estimated from the proportion between the continuously monitored site Q and the Q on glacier snout streams on corresponding dates. Arithmetic mean was found appropriate due to no correlation between c and Q in any site. For flux calculation purposes, c values below LOD were assumed to be equal to half of the LOD.

## 3. Results

The deposition of both species in snow was highly variable (Fig. 1), with outliers potentially dominating the vertical pattern. Overall, the sum of phenols supply was diminishing with decreasing elevation on the glacier, while the opposite was true for formaldehyde. Since the lower part of the glacier melts first, this

might be connected to a difference in species behavior (formaldehyde can be both a product of and subject to photochemical degradation [6], phenols are most likely to be photodegraded).

In the proglacial river, the proportion of HCHO supplied from the glacier was diminishing during the season (Fig. 2a), with the 16th August value being unexpectedly high. In the case of phenols (Fig. 2b), the picture is less clear, with exceptionally high output occurring in F3 site on 23rd July, and a period of elevated proglacial runoff (site F1) between 31st July and 8th August, unmatched by the snout stream contents together. These imbalances stress the influence of the glacier forefield on phenol runoff temporal distribution from glaciated catchments.

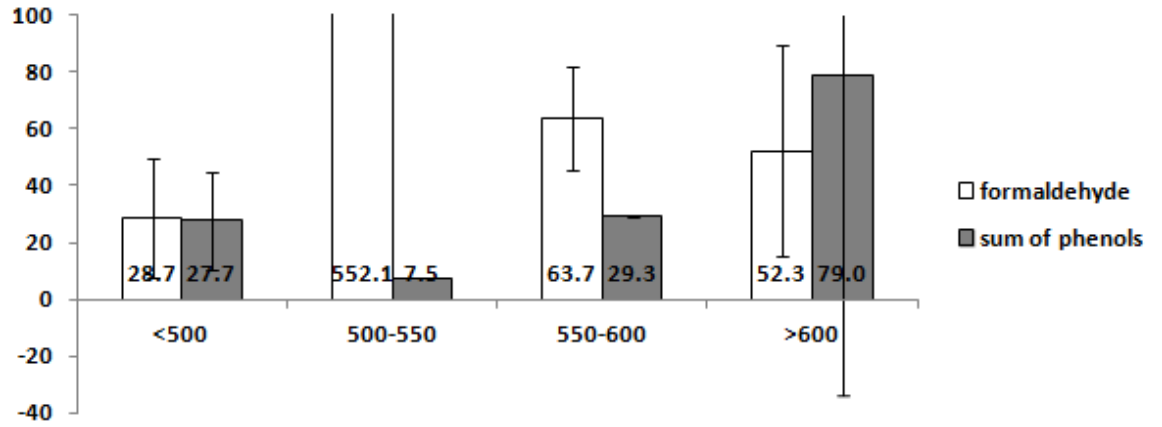


Fig. 1. Snow content of formaldehyde and phenols in elevation bands [m asl] upon glacier surface. Error bars indicate one standard deviation between samples where more than one location was sampled.

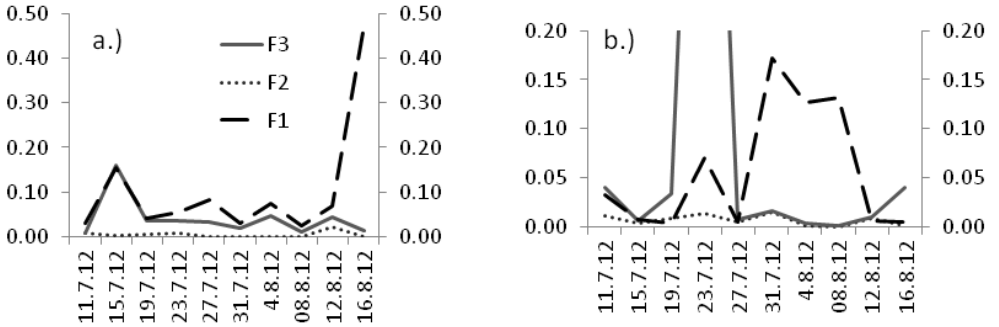


Fig. 2. Total runoff of HCHO (a) and phenols (b) in both proglacial streams (cumulative graph for these two only) as compared to the proglacial site runoff.

If the snow input is balanced against meltwater output at the glacier snout, a net release of both formaldehyde and phenols occurs (Table 1). This could have been supplied either from summer atmospheric deposition, glacier ice melt, or most probably both. Refreezing processes have been rather inefficient in capturing both species, as superimposed ice contained approximately 10% of the snow input of these chemicals (0.008 g · $m^{-2}$ for formaldehyde and 0.006 g · $m^{-2}$ for phenols), whilst it stored 29% of the snow water equivalent at the same time.

There was a marked increase in both species removal on the 250 m stretch (164% for HCHO and 48% for phenols, the corresponding water runoff increase being 51%). This indicates an important role of the glacier forefield in producing high quantities of formaldehyde in runoff.

Table 1. Formaldehyde and phenol inputs and outputs upon Foxfonna glacier in the summer 2012 (in brackets average deposition in g · $m^{-2}$).

| Flux [$10^6$ g] | Formaldehyde | Σphenols |
|---|---|---|
| Snow deposition | 0.138 (0.087) | 0.086 (0.054) |
| Meltwater output (glacier snout, F2+F3) | 0.244 | 0.341 |
| Meltwater output (including icing, F1) | 0.643 | 0.506 |
| Budget sum | -0.106 | -0.255 |

## 4. Discussion

Since formaldehyde and phenols are both mobile chemicals, their variable distribution in snow is most probably an indicator of melt processes that were not yet widespread at the time of sampling. Whilst melting, 90% of the deposition was removed, with refreezing being inefficient to capture these mobile species. The superimposed ice content of these chemicals was only measured in one site, nevertheless this was the site with high total organic carbon (TOC) storage in the refrozen ice layer (data not shown, further information will be provided in a forthcoming paper), so the contrast between these species and TOC behaviour is noticeable. An important process leading to fast removal of formaldehyde might be its photoxidation, as 24 hours of exposure to UV light has been shown to remove 90% of the initial HCHO concentration [12].

A part of the glacial system that seems to most influence the formaldehyde and phenols release is the glacial forefield. This part is built of refrozen outflow, most probably groundwater, with a high content of clay minerals that can act as adsorption media. It is also an exposed former glacier bed, given the recent deglaciation of the area. Formaldehyde is known for its physisorption on ice crystals in snow [7], [13] and to adsorb on silicate materials [14], hence it can be stored in vast amounts in the glacier forefield. Adsorption simulation shows that formaldehyde is most effectively adsorbed in the layers closer to the adsorbent grain, and later on during the layer development, other compounds (e.g. methanol) prevail [13]. This can protect HCHO from changeable release dynamics. Only at the end of the melt season is there a possibility for more dynamical behaviour (although the one sample at the end of the season might also be an outlier result).

Clay minerals are known to adsorb phenols as well [15], nevertheless the dynamics of this compound group in the glacier forefield is more complicated than that of formaldehyde, with peak runoff happening earlier in the season. This is surprising, given the higher solubility in water of formaldehyde, and it may be attributed to differences in mobility between particular species within the compound group. Published simulations of phenol behaviour report dependency of adsorption rate on pH [15], however in the environmental data presented here, this is not the case. There was not found to be a relationship between phenols concentration or phenols flux with pH value. The concentrations of phenols encountered in the field are also 3 orders of magnitude lower than in the laboratory study cited here [15].

## 5. Conclusion

Both formaldehyde and phenols are highly mobile in the glacial settings, refreezing processes influencing them only to a small extent. However, if incorporated into glacial ice from snow, they will be released at an increased pace. As a result of deglaciation, former glacial beds become exposed as glacier forefields, which

play a major role in both formaldehyde and phenol dynamics. The processes causing changes in these species' fluxes are yet unknown, but it is highly probable that adsorption on clay mineral particles is an important factor.

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## References

[1] Moholdt G., Nuth C., Hagen J. O., Kohler J. Recent elevation changes of Svalbard glaciers derived from ICESat laser altimetry. *Remote Sens Environ* 2010; 114, 11, 2756–2767.

[2] Gardner A. S., Moholdt G., Wouters B., Wolken G. J., Burgess D. O., Sharp M. J., Cogley J. G., Braun C., Labine C. Sharply increased mass loss from glaciers and ice caps in the Canadian Arctic Archipelago. *Nature* 2011; 473, 7347, 357–60.

[3] Stubbins A., Hood E., Raymond P. A., Aiken G. R., Sleighter R. L., Hernes P. J., Butman D., Hatcher P. G., Striegl R. G., Schuster P., Abdulla H. a. N., Vermilyea A. W., Scott D. T., Spencer R. G. M. Anthropogenic aerosols as a source of ancient dissolved organic matter in glaciers, *Nat Geosci* 2012; 5, 3, 198–201.

[4] Bogdal C., Schmid P., Zennegg M., Anselmetti F. S., Scheringer M., Hungerbühler K. Blast from the past: melting glaciers as a relevant source for persistent organic pollutants, *Environ Sci Technol* 2009; 43, 21, 8173–7.

[5] Wasi S., Tabrez S., Ahmad M. Toxicological effects of major environmental pollutants: an overview., *Environ Monit Assess* 2013; 185, 3, 2585–93.

[6] Grannas A. M., Jones A. E., Dibb J., Ammann M., Anastasio C., Beine H. J., et al. An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos Chem Phys* 2007; 7, 4329–73.

[7] Hutterli M. A. Sensitivity of hydrogen peroxide ($H_2O_2$) and formaldehyde (HCHO) preservation in snow to changing environmental conditions: Implications for ice core records, *J Geophys Res* 2003; 108, D1, 4023.

[8] Fellman J. B., Spencer R. G. M., Hernes P. J., Edwards R. T., D'Amore D. V., Hood E. The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems, *Mar Chem*, 2010; 121, 1–4, 112–122.

[9] Campbell A. N., Campbell J. R. Concentrations, Total and Partial Vapor Pressures, Surface Tensions and Viscosities, in the Systems Phenol-Water and Phenol-Water-4% Succinic Acid, *J Am Chem Soc* 1937; 59, 12, 2481–2488.

[10] Hodson A. J., Anesio A. M., Tranter M., Fountain A., Osborn M., Priscu J. C., Laybourn-Parry J., Sattler B. Glacial Ecosystems, *Ecol Monogr* 2008; 78, 1, 41–67.

[11] Margesin R., Moertelmaier C., Mair J. Low-temperature biodegradation of petroleum hydrocarbons (n-alkanes, phenol, anthracene, pyrene) by four actinobacterial strains, Int Biodeter Biodegr 2013; 84, 185–191.

[12] Jacobi H.-W., Annor T., Quansah E. Investigation of the photochemical decomposition of nitrate, hydrogen peroxide, and formaldehyde in artificial snow, *J Photoch Photobio A* 2006; 179, 330–338.

[13] Cuppen H. M., van Dishoeck E. F., Herbst E., Tielens A. G. G. M. Microscopic simulation of methanol and formaldehyde ice formation in cold dense cores, *Astron Astrophys* 2009; 508, 1, 275-287.

[14] Srisuda S., Virote B. Adsorption of formaldehyde vapor by amine-functionalized mesoporous silica materials, *J Environ Sci* 2008; 20, 379–384.

[15] Banat F. A., Al-bashir B., Al-asheh S., Hayajneh O. Adsorption of phenol by bentonite, *Environ Pollut* 2000; 107, 391–398.